In-situ reactive blending of polyethylene and polypropylene in co-rotating and counter-rotating extruders

Hettema, R; Van Tol, J.; Janssen, L.P.B.M.

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In-Situ Reactive Blending of Polyethylene and Polypropylene in Co-Rotating and Counter-Rotating Extruders

R. HETTEMA, J. VAN TOL, *and* L. P. B. M. JANSSEN*

Department of Chemical Engineering
University of Groningen
9747 AG Groningen, The Netherlands

Blends of high-density polyethylene (HDPE) and polypropylene (PP) were prepared in different twin-screw extruders. Two additives, a peroxide initiator and a polymerizable monomer, were added to the polymeric feed components. A large influence on the physical properties, such as toughness and impact strength, and on the morphology was observed. Reactive extrusion substantially improves mechanical properties: a three-fold increase of elongation at break and doubling of the impact strength. Variation of extruder settings also had a large influence on the product; the final properties were improved when the shear rate was raised, but sufficient residence time is necessary in reactive compatibilization. Scanning electron micrographs of the fracture surfaces of blends indicate a refinement of the surface structure.

INTRODUCTION

The steady growth in the use of plastic materials in packaging applications has caused problems in solid waste disposal. Therefore, plastic recycling has become necessary. Plastic material recycling programs mainly aim at recycling of post-consumer reclaim plastics of packaging items. With continuous refinement in the quality and decreasing cost of recycling, recycled polymers should gain significance as feed stocks for a wide range of products and applications.

High-density polyethylene (HDPE) is a primary packaging material for disposable bottles and one of the most commonly recycled plastics. One of the problems that occur with HDPE waste is the contamination with polypropylene (PP) coming from closures or sprouts. Because of the immiscible nature of the components, both in the melt as well as in the solid state, resulting blends show a deterioration in impact performance and tensile properties (1).

The majority of polymers found in waste plastic streams unfortunately form a phase-separated morphology. Because ductility and impact strength are important properties for polymers, an effective method for the compatibilization of the blend is needed to improve these properties. Compatibilization usually is promoted through the addition of block or graft copolymers with segments capable of interacting with the blend constituents (2, 3). These copolymers lower the interfacial tension and improve adhesion between the matrix and the dispersed phase. Kroeze *et al.* (4) successfully used a "living" free radical polymerization technique instead of conventional anionic techniques to accomplish the synthesis of such block copolymers used for compatibilization.

An attractive alternative is chemical modification of a blend by reactive extrusion (5) which can be a relatively cheap approach for improvement of the properties of a polymer blend (6). In a recent paper, Hu (7) performed both grafting of PP with glycidyl methacrylate and blending with PBT in a one-step extrusion process. The mechanical properties of the resulting blends were superior compared to the uncompatibilized blend. Fellahi et al. (8) have improved the stress at break and the impact strength of mixed plastics simply by processing it in the presence of a dialkyl peroxide. These improvements are most likely due to the formation of copolymers acting as compatibilizer by recombination of macroradicals. In addition, a reduction of the rheological mismatch for a blend containing low viscosity PE and high viscosity PP can enhance dispersive mixing. This is caused by the preferred reaction of these polymers with peroxide. The PE phase has a tendency for crosslinking (9), whereas PP with a peroxide mainly results in chain scission. Randall *et al.* (10) describe the preparation of impact modified PP blends by treating a reactor blend of PP and LLDPE with a peroxide. Various fragments will be present and recombine to form block or graft

*To whom correspondence should be addressed.

Table 1. Material and Molecular Properties of Extruded Virgin HDPE and PP.

Material	Tensile Strength (Mpa)	Elongation at Break (%)	Young's Modulus (Mpa)	Notched Izod Impact Strength (kJ/m^2)	M_n	M_w
HDPE	23.1	471	795	12.8	21,000	228,000
PP	37	100	1300	3	44,000	188,000

materials. This method increases the Gardner impact strength by 30%.

Teh *et al.* (11) have concluded that one of the main problems in the modification of PE/PP blends with peroxide is the difficulty in controlling the degradation of the PP. These unwanted side reactions, such as chain scission and disproportionation, can be suppressed by addition of an unsaturated monomer (12). One function of these low molecular weight compounds is to promote the formation of copolymers (random, block or graft) resulting in improved compatibility. The monomer can stabilize the polyolefin macro radical sites (13) formed by the peroxide radicals, and create interchain block or graft copolymers by recombination. Another function of the monomer could be that of a vector fluid (14). This fluid is preferentially immiscible with both phases and carries the reactive ingredients to the interface. If the vector fluid is a polymerizable monomer, both polymers could obtain the same grafts, resulting in stronger interactions at the interface (15).

The low molecular weight compounds used in reactive extrusion are usually added at relatively low concentrations. For that reason they offer considerable economic advantages versus polymeric compatibilizers that are more expensive and usually only effective at higher concentrations.

This paper describes research into reactive blending of HDPE and PP in counter-rotating and in self-wiping co-rotating extruders. Tensile behavior, impact properties, the morphological structure, and thermal properties are studied. It should be realized that this is a model system with pure components and that in a typical commingled bottle stream a variety of contaminants can be found, such as screen printed or heat transfer labels, which cannot be removed by washing. These additives may influence the reactivity of the peroxide and the monomer.

EXPERIMENTAL

Selection of Blend Components

The HDPE used in these experiments was blow-molding/extrusion grade (Stamylan HD 9630, DSM) with a density of 961 kg/m^3 and a melt flow index, MI (2.16 kg, 190°C) = 0.35 dg/min. The PP was isotactic homopolymer in the form of a porous granule (Accurel EG 100, MI (2.16 kg, 190°C) = 21 dg/min, AKZO-Nobel, manufactured from Moplen Z30S, Montell). Mechanical and molecular properties of both polymers are given in *Table 1*. The organic peroxides were 2,5-bis(tert-butylperoxy)-2,5-dimethylhexane (Trigonox 101, AKZO-Nobel) and 2,5-bis(tert-butylperoxy)-2,5-dimethylhexyne (Trigonox 145E85, AKZO-Nobel). Dissociation constants, Arrhenius parameters, and half-life times of these peroxides are given *Table 2*. The monomer was n-butyl methacrylate (Interorgana) and all components were used without further purification.

Extrusion System

Two different extruders were used for processing. A tumble mixed blend of HDPE and PP was fed, using a K-Tron screw feeder, into an APV-Baker co-rotating twin-screw extruder with L/D = 24 and D = 50 mm or a Rollepaal counter-rotating closely intermeshing twin-screw extruder with L/D = 15 and D = 40 mm. All blends were extruded with a flat temperature profile of 180°C applied across all zones. To avoid bridging in the entrance, the feed zone was cooled (Rollepaal) or set at 120°C (APV-Baker). The screw configuration of the APV-Baker and the Rollepaal extruder are shown in *Fig. 1*.

Of the several options for dosing the reactants into the extruder, two were used. The peroxide and the monomer were absorbed in the porous PP, which subsequently was tumble mixed with HDPE before feeding to the extruder. This method is described by Vander Wal *et al.* (16). Another method used was feeding the reactants at the same feed port as the solid feed, using a positive displacement pump. After extrusion the mixture was frozen in liquid nitrogen to preserve the morphology obtained and to stop any reactions taking place. Further reactions could take place during sample preparation but because of the very low concentration of reactants still present in the sample (less than 0.5 mass%), no significant influence on mechanical properties is assumed.

Characterization

The specimens for mechanical tests were compression molded at 180°C with a hydraulic 20-ton press, and tests were performed following the standard

Table 2. Dissociation Constants and Arrhenius Parameters of Trigonox 101 and Trigonox 145.

Material	K0 (s^{-1})	Ea (J/mol)	$\tau_{1/2}$ @ 180°C
Trigonox 101	1.68E+16	155,490	35
Trigonox 145	1.90E+15	150,670	86

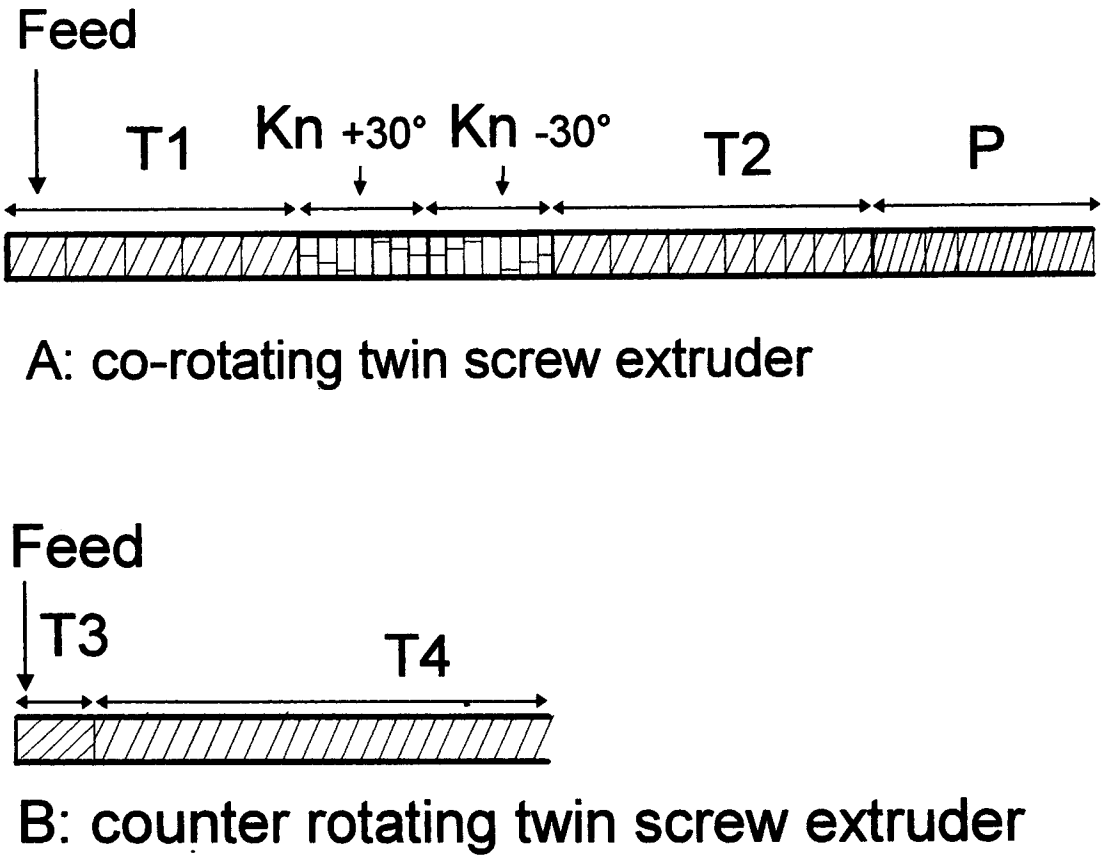

Fig. 1. A: Screw layout for experiments in the co-rotating extruder. T1 = 0.38 m transporting section, Kn 30° = 0.09 m kneading section with 30° forwarding angle, Kn -30° = 0.09 m kneading section with 30° reversed angle, T2 = 0.48 m transporting section, P = 0.15 m pressure buildup section. B: Screw layout of the experiments in the counter-rotating extruder. T3 0.15 m feed section, T4 = 0.45 m transporting section.

ASTM procedures. Tensile tests according to ASTM D1708 were performed on an Instron, using specimens of 2 mm thickness and a crosshead speed of 10 mm/min. Impact properties were measured according to ASTM D256 with notched bars of 4 mm thickness. All tests were performed at room temperature and at least five measurements were made to obtain averages. The error as depicted by the error bars in *Figs. 4, 5* and *7* to *12* are ±4% for the modulus measurements, ±9% for the impact measurements and ±5% for the measurements of the elongation at break.

Thermal properties were measured by a differential scanning calorimeter (DSC 7, Perkin Elmer). To remove thermal history, samples were first heated to 200°C. The crystallization temperature (T_c) was measured during the subsequent cooling to room temperature. Crystalline melting temperature (T_m) and heat of Fusion (ΔH_f) were measured during the second heating cycle. The scan speed was 10°C/min. The dynamic viscoelasticity (DMTA) tests were done in a Reometrics RSA-2. The frequency was 1 Hz and the temperature rise was 1°C/min. The flow properties of the virgin materials were measured in a Göttfert HKV 1000/1600 rheometer at 190°C. Dynamic viscosimetry was performed on a Bohlin rheometer using parallel-plate geometry (radii of specimens: 25 mm). The experiments were also carried out at 190°C.

High Temperature Size Exclusion Chromatography (Waters 150C) using 1,2,4 trichlorobenzene as a solvent was used to characterize the molecular weight distribution of the samples. Universal calibration was made with monodisperse polystyrene standards. Electron microscopy was performed on plasma-etched, nitrogen-fractured specimen. The magnification is 10,000, with a tilt angle of 6°.

RESULTS AND DISCUSSION

Rheology

The complex viscosity of the starting materials as a function of the frequency ω as measured by parallel plate rheometry and the viscosity as a function of the shear rate $\dot{\gamma}$ are plotted in *Fig. 2*. The non-Newtonian behavior of the two polymers is clearly visible. In this case, HDPE is the major component, and its viscosity is higher than the viscosity of the PP. The viscosity ratio p decreases from 1 at 0.001 s^{-1} to 0.23 at 400 s^{-1}. The average shear level in the extruder channel was 20 to 75 s^{-1} and the shear rate for material passing the flight was 120 to 400 s^{-1} during our experi-

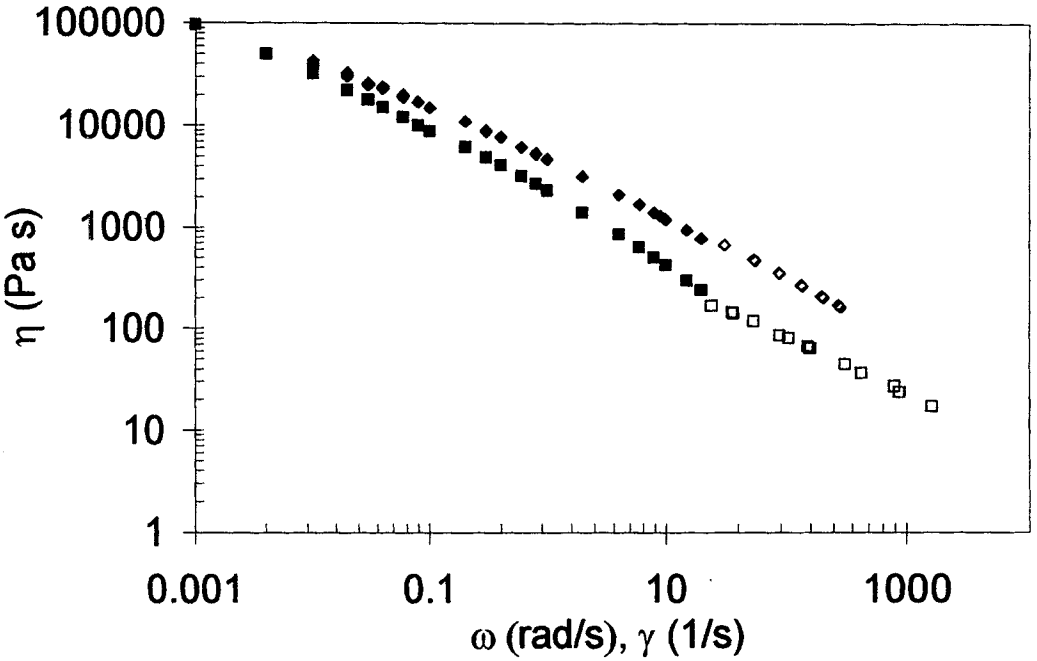

Fig. 2. Viscosity of HDPE (◆, ◇) and PP (□, ■) as a function of frequency and shear rate at 190°C.

ments; for practical purposes capillary rheometry data are sufficient. It becomes obvious that in this case crosslinking of the HDPE phase and degradation of PP cannot improve mixing, and therefore are highly undesired reactions.

Extrusion

Extrusion and melt blending influence the stress-strain behavior and the impact strength of a polymer or polymer blend. *Figure 3* shows the stress-strain behavior of unextruded HDPE, and HDPE extruded in a counter rotating and in a co rotating twin screw extruder. All samples showed yielding at around 11% strain. It is clearly visible that extrusion increases the strain at break. This effect is slightly larger in the counter-rotating extruder than in the co-rotating extruder. *Figure 4* shows the dependence of the impact strength and elongation at break as a function of the percentage PP in the blend for a physical blend without compatibilization. These measurements are used as reference. In our case, negative deviation is observed for all properties, as expected in the case of an immiscible blend. Increasing the amount of PP resulted in a slightly increased Young's modulus. These results are consistent with results published by several authors (17, 18). The performances of both extruders are quite similar in this case; the impact strengths are comparable but at low concentrations of PP, the toughness is better in a co-

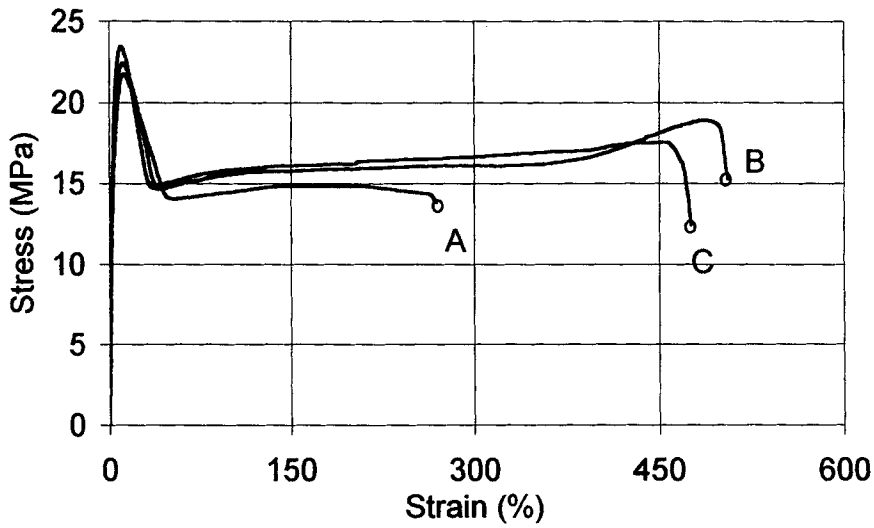

Fig. 3. Uniaxial stress-strain curves of: (A) unextruded HDPE; (B) HDPE counter-rotating-TSE; Q = 1.25E-3 kg/s, N = 0.67 rps (C) HDPE co rotating-TSE, Q = 3.6E-3 kg/s, N = 1.8 rps. o = Point of rupture.

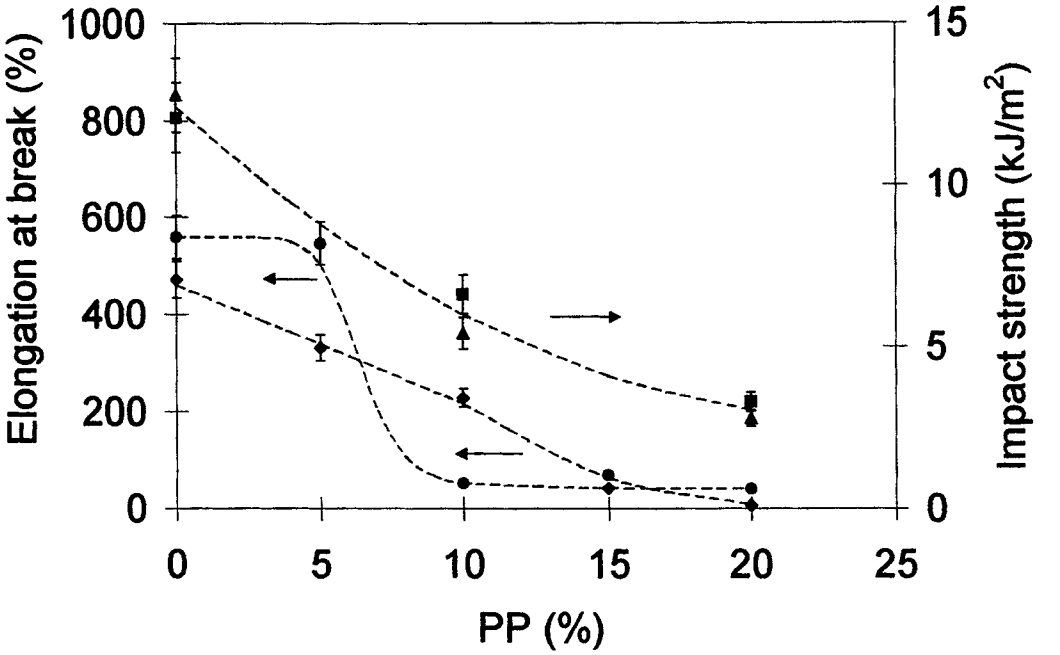

Fig. 4. Effect of increasing amount of polypropylene on the notched Izod impact strength and elongation at break for a HDPE/PP mixture. Co-rotating-TSE, Q = 3.6E-3 kg/s, N = 1.8 rps; ◆ elongation at break (%), ■ impact strength (kJ/m²). Counter rotating-TSE, Q = 1.25E-3 kg/s, N = 0.67; ● elongation at break (%), ▲ impact strength (kJ/m²).

rotating extruder. All experiments described in the next sections were performed with a mixture of 90 weight% HDPE and 10 weight% PP.

Extrusion With Peroxide Only

The addition of a peroxide (Trigonox 101) only to a mixture of 90 weight% HDPE and 10 weight% PP by adsorbing it in the porous PP, leads to a strong deterioration of mechanical properties (*Fig.* 5). At peroxide concentrations below 0.05 weight%, based on the total mass of polymer, a decrease in strain at break and impact strength is observed. Cheung *et al.* (19) also found for blends of LLDPE and PP, a strong decrease in impact strength with increasing peroxide

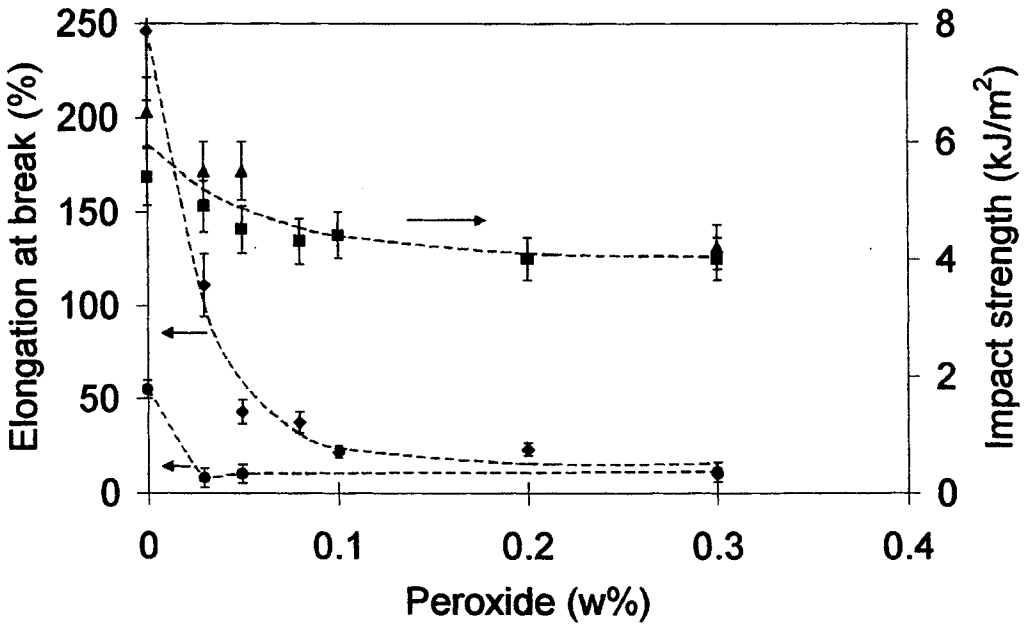

Fig. 5. Effect of increasing peroxide concentration on the notched Izod impact strength and elongation at break for a 90 HDPE/10 PP mixture. Co-rotating-TSE; Q = 3.6E-3 kg/s, N = 1.8 rps; ● elongation at break (%), ■ impact strength (kJ/m²).Counter-rotating-TSE, Q = 1.25E-3 kg/s, N = 0.67; ● elongation at break (%), ▲ impact strength (kJ/m²).

concentrations. Moreover, at higher concentrations of peroxide, crosslinking of the HDPE phase is predominant resulting in a strong increase of the die-pressure and the torque. The viscosity of HDPE is higher than the viscosity of PP and the reaction thus enlarges the viscosity difference in this way, thereby resulting in poorer mixing. Xanthos *et al.* (20, 21) published experimental data on influencing the viscosity ratio of an LDPE/PP (25/75) mixture by peroxides, which resulted in a mixture of highly degraded PP with a branched or crosslinked LDPE.

The way peroxide was introduced into the blend had little effect on the trends observed. Both methods of dosing—by adsorption and by means of a pump—showed negative effects. This was observed in both types of extruders.

Extrusion With Peroxide and Monomer

The Influence of Different Amounts of Peroxide and Monomer

Introducing both monomer and peroxide to a polymer blend improves the mechanical properties. A constant initial amount of 2 wt% of n-BMA, based on the total amount of polymer, and a variable amount of peroxide (T101) to a mixture of HDPE and PP leads to an optimum in properties measured. However, increasing the initiator concentration is limited by the occurence of crosslinking at concentrations above 0.3 wt%. Already at low initiator concentrations, toughness increases considerably but at higher concentrations toughness decreases again, as shown in *Fig. 6.* The results for both extruders are comparable.

A relatively high concentration of n-BMA will lead to more monomer radicals, which will result in homopolymerization rather than grafting on the polyethylene or polypropylene. At relatively low concentrations of n-BMA, the initiator dissociation can lead to higher concentrations of macroradicals, which can react with a monomer unit. The influence of both effects on mechanical properties is shown in *Fig. 7.* This reaction can be followed either by homopolymerization of the n-BMA or crosslinking with another macroradical. A combination of homopolymer BMA and grafted BMA is reported to attribute positively to the impact strength as well (22). Extraction of several reactive extruded samples by solution/precipitation showed that conversion of monomer was over 65% and depended on the amount of peroxide added. The ratio of homopolymer/grafted polymer is 1.25 so slightly more homopolymer is formed during the process.

In the following three sections, the extrusion parameters screw speed, throughput, and die-resistance were varied. The extruder feed consisted of a 90/10 HDPE/PP mixture with 2 mass% n-BMA and 0.05 mass% Trigonox 101 absorbed in the porous polypropylene. The influence of operating conditions on mechanical properties in both type of extruders shows the same tendencies as reported in reactive extrusion of methacrylates (23, 24)

The Influence of the Throughput

Increasing the throughput in the counter-rotating extruder, keeping all other parameters constant, caused a strong decrease in elongation at break (*Fig. 8*). The notched impact strength and the Young's modulus reach an optimum. At the optimum, the product showed signs of crosslinking. The increased throughput has a negative influence not only on the residence time in counter-rotating extruders but also on the mixing efficiency. This mixing efficiency is defined as the average number of times a fluid element is subjected to the high shear fields in the leakage gaps.

$$E = \frac{v_f Q_l}{2Q} \tag{1}$$

where v_f is the number of filled chambers, Q_l the total of leakage flows, and Q the throughput (25). Moreover,

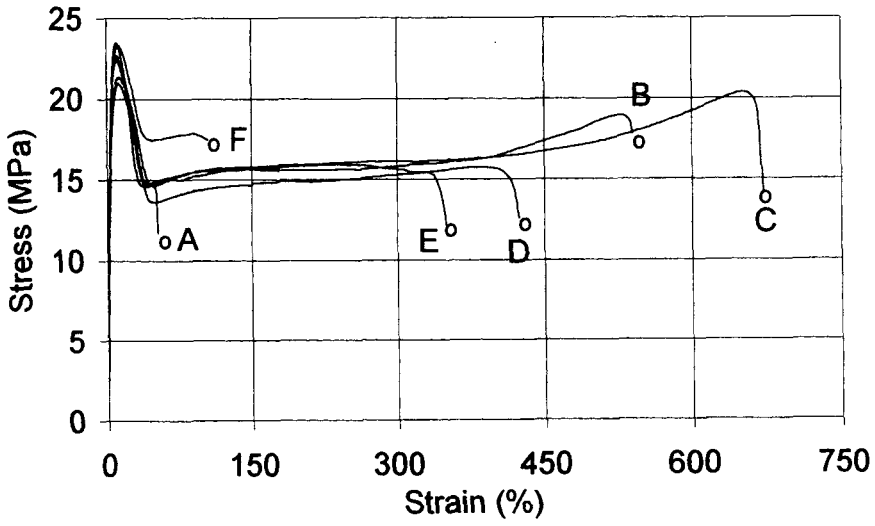

Fig. 6. Effect of increasing peroxide concentration on the stress-strain behavior of a 90 HDPE/10 PP mixture with 2 w% BMA in a counter-rotating twin screw extruder Q = 1.25E-3 kg/s, N = 0.67 rps. (A) 90/10 HDPE/PP (reference value), (B) 0.01 w% T101, (C) 0.05 w% T101, (D) 0.1 w% T101, (E) 0.29 w% T101, (F) 0.49 w% T101. o = Point of rupture.

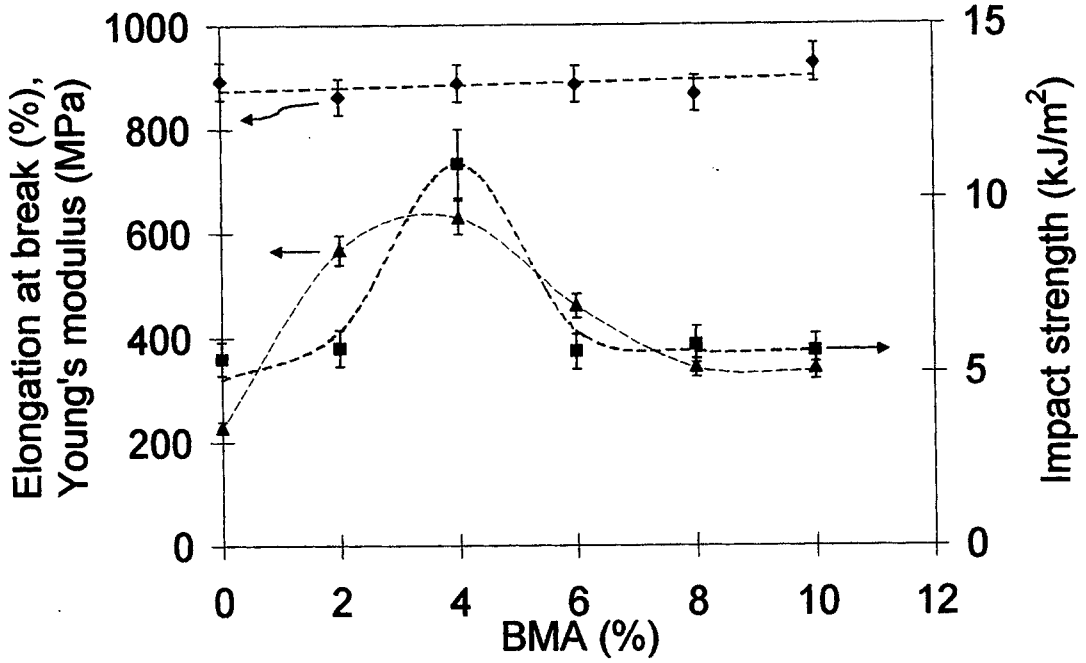

Fig. 7. Effect of increasing BMA concentration for a co-rotating twin screw extruder on elongation at break (▲) Young's modulus (◆) and impact strength (■). Monomer/initiator ratio is 40, Q = 3.6E-3 kg/s, N = 1.8 rps.

a minimal amount of residence time is also an important factor for the compatibilizing effect.

In the co-rotating extruder, the effect of variation of the throughput on the stress-strain behavior is less pronounced. In this type of extruder all material passes a high shear zone. An increased throughput will therefore less affect the mixing capacity. As can be seen in *Fig. 9*, the modulus is unaffected by changing the throughput while the elongation at break and the impact strength improve. Moreover, the overall properties of the mixtures are ameliorated compared to the counter-rotating mixtures. At the throughput used, the extruder has a low degree of fill, ranging from 0.11 to 0.35 in the extruder channel. Increasing the feed ratio

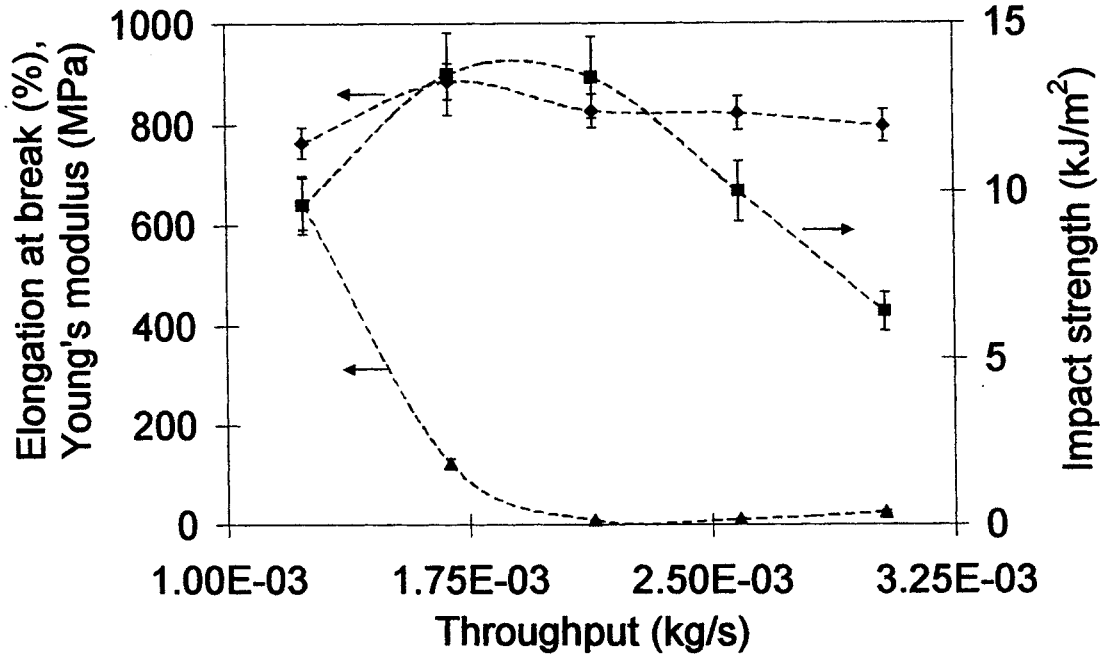

Fig. 8. Effect of variation of throughput in a counter-rotating twin screw extruder on elongation at break (▲) Young's modulus (◆) and impact strength (■); N = 0.67 rps.

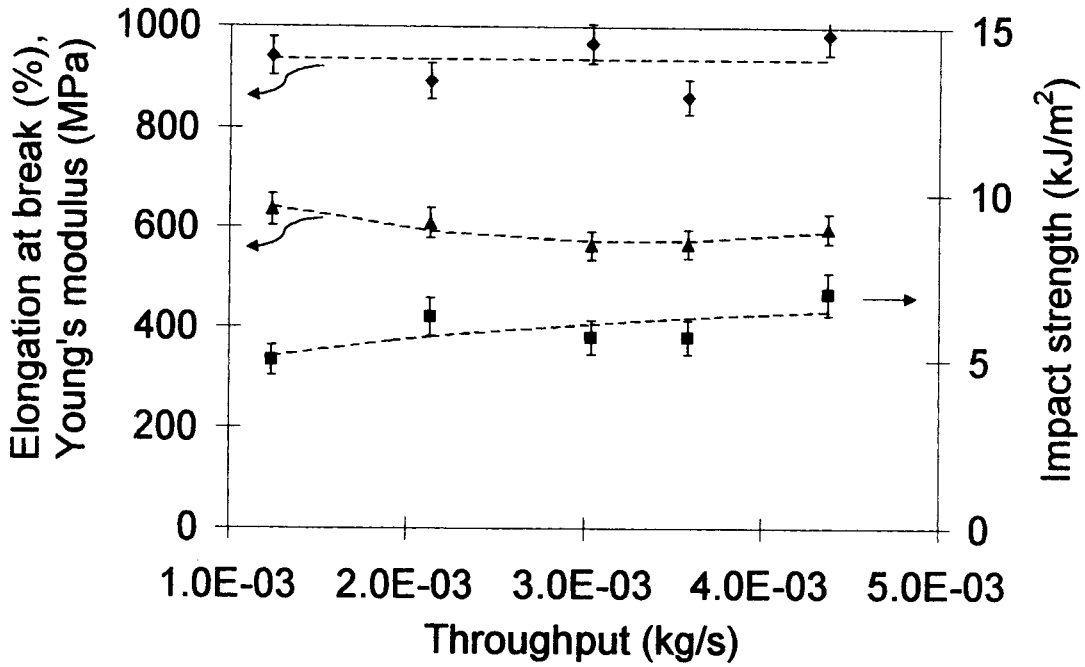

Fig. 9. Effect of variation of throughput in a co-rotating twin screw extruder on elongation at break (▲), Young's modulus (◆) and impact strength (■), N = 1.8 rps.

results in higher shear forces on the material hence more intensive mixing.

Influence of the Screw Speed

From the experiments in a counter rotating twin screw extruder it can be concluded that an increase in rotation rate of the screws at constant throughput has a positive influence on the impact strength (*Fig. 10*). Despite the fact that an increased screw speed results in a slight decrease of mean residence time, due to a decrease in the fully filled length, the mixing efficiency of the components increases, resulting in increased impact properties. Therefore the influence of the mixing is dominant in this area investigated. At a higher screw

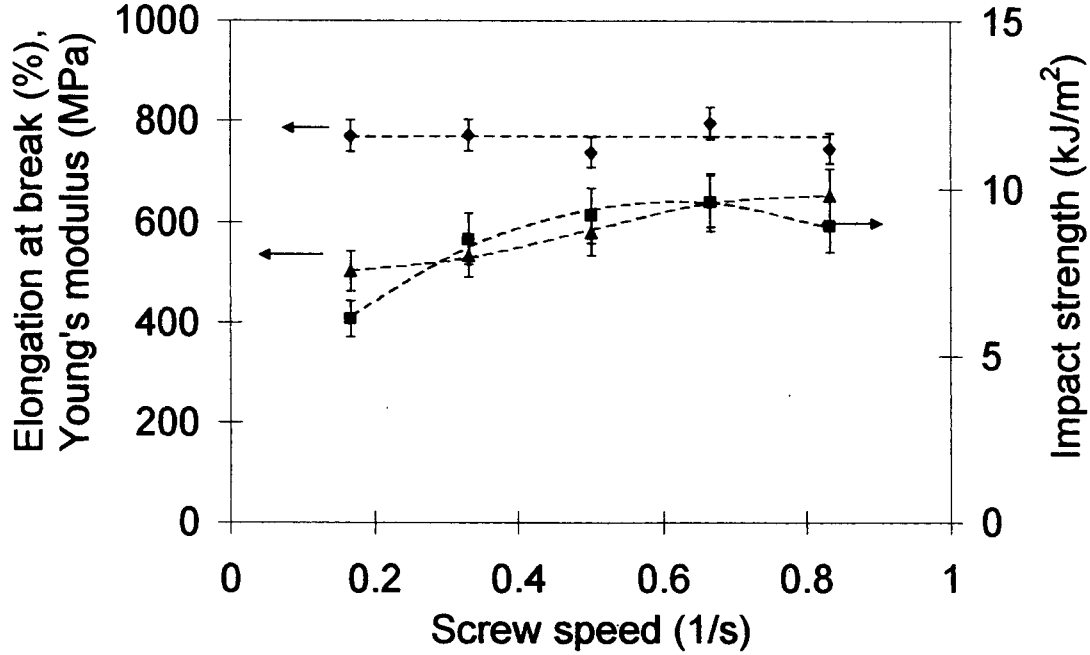

Fig. 10. Effect of variation of screw speed of a counter-rotating twin screw extruder on elongation at break (▲), Young's modulus (◆) and impact strength (■); Q = 1.25E-3 kg/s.

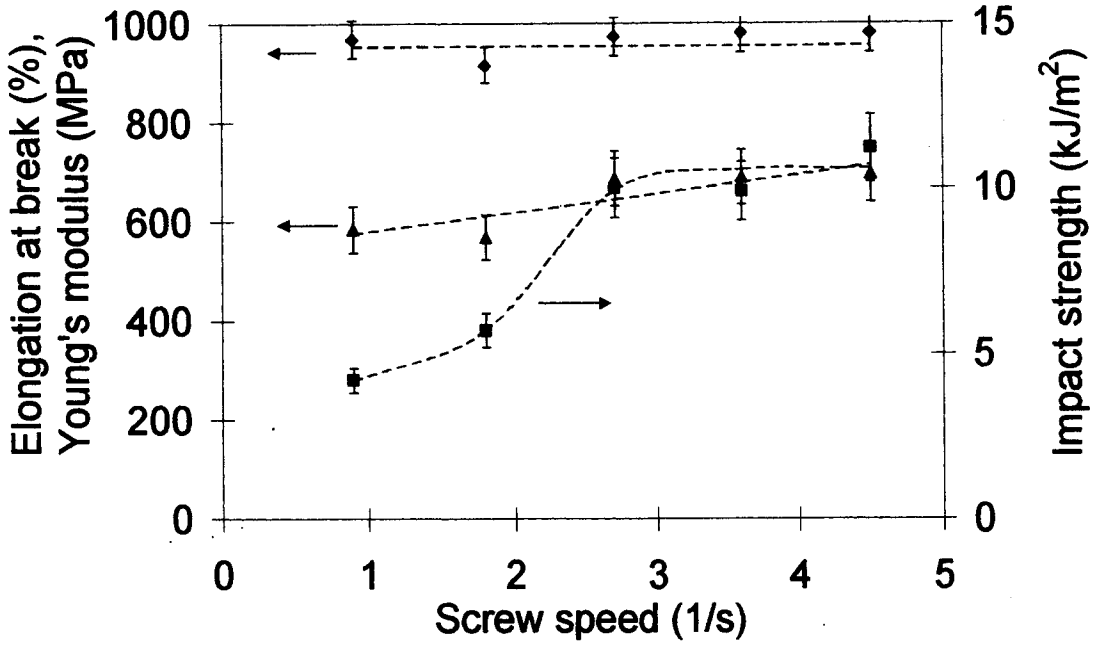

Fig. 11. Effect of variation of screw speed of a co-rotating twin screw extruder on elongation at break (▲), Young's modulus (◆) and impact strength (■); Q=3.6E-3 kg/s.

speed the influence of the decreased residence time becomes noticeable and there is no further increase in properties. The starting point of the reaction is also affected by the screw speed because melting will start later in the extruder, leaving less time for reaction.

In a co-rotating extruder (*Fig. 11*) the Young's modulus is not affected by screw speed, but the absolute value is 25% higher than the material processed on the counter-rotating twin-screw extruder. The strain at break and the impact strength also increase with a higher screw speed, yet there is little effect of the diminished residence time. The residence time of the counter-rotating extruder as estimated from breakthrough experiments is 120 s, in the co-rotating extruder 280 s. In this time, 92% and 100%, respectively of the initiator will be decomposed.

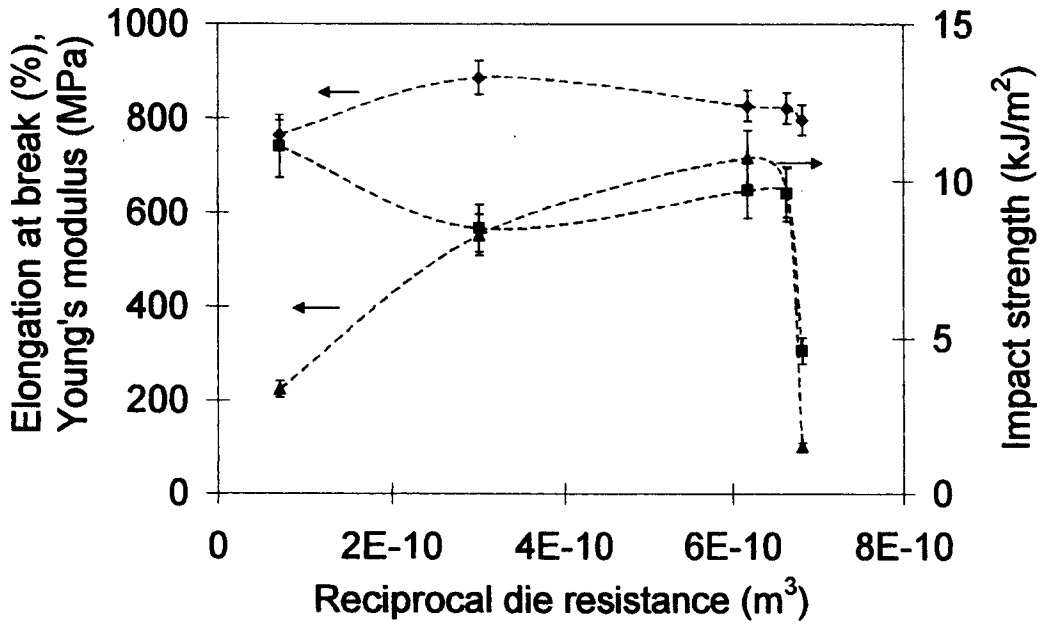

Fig. 12. Effect of variation of reciprocal die resistance of a counter-rotating twin screw extruder on elongation at break (▲), Young's modulus (◆) and impact strength (■), Q = 1.25E-3 kg/s, N = 0.67.

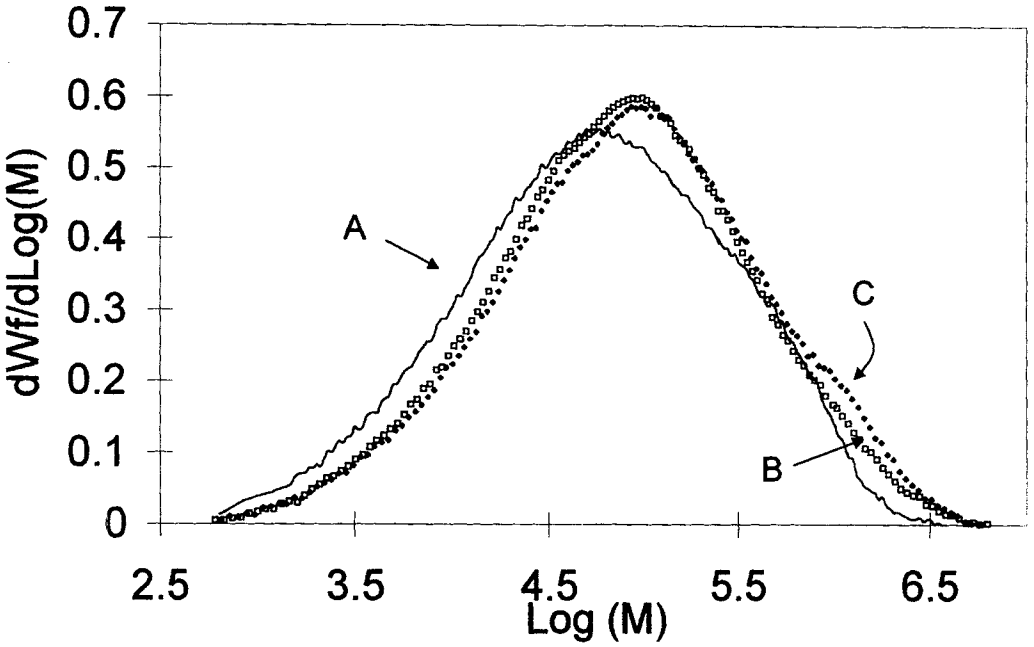

Fig. 13. Molecular weight distribution curves of a HDPE/PP 90/10 blend processed without peroxide (A), with 2 m% BMA and 0.05 m% T101 (B), and with 0.05 m% T101 (C).

The Influence of the Die-Resistance

A feature available on our counter-rotating twin-screw extruder was an adjustable die with a quantified die-resistance. The die-resistance has strong influence on the stress-strain behavior of the resulting blend (*Fig. 12*). It not only determines the fully filled length, but also creates elongational flows, resulting in a reduction of dispersed phase diameter (26). Sufficient reaction and intimate mixing should result in a blend with improved properties (27). The number of fully filled chambers on the screw was calculated, and as soon as one single chamber per screw is fully filled, optimal mechanical properties could be reached. Ebner and White (28) also found with PP degradation by peroxide, in a similar extruder without shearing elements, that all degradation occurred in the neighborhood of the die.

Molecular Properties

In addition to other variables, a change in mechanical properties can be attributed to changes in molecular weight. *Figure 13* shows the molecular weight distribution of a blend and two reactive extruded samples, one with a combination of BMA and peroxide and one with peroxide only. Because of the high dispersity of the HDPE and the relatively low content of the PP no separate weight fraction was observed. The M_w of the PP is 188,000 g/mol, so log (M) is 5.27. Clearly visible is the overall shift of the distribution towards higher molecular weights, which is to be expected in case of branching or crosslinking of the HDPE. Degradation of the PP is not clearly visible, but because the increase of the weight fraction between log (M) 4.75 and 5.5, it is assumed the PP undergoes some chain scission. This increase cannot explain the entire increase, so crosslinking of medium molecular weight HDPE also has to be taken into account. The molecular weight distribution of the reactive extruded sample without monomer shows a much higher fraction of molecular weights between 1,100,000 and 2,500,000. Reactive extrusion with addition of monomer combined with peroxide also results in a slight increase in high M_w but to a much lesser extent than when only peroxide is added.

Thermal Properties

The 90/10 HDPE/PP blend was further analyzed on thermal properties by DSC and through dynamic mechanical thermal analysis (DMTA) over a wide temperature range.

The damping factor (tanδ) as a function of the temperature (*Fig. 15*) shows no increase in the PP damping peak as a result of the addition of monomer and peroxide initiator. Shifting of the location of this peak is usually associated with improved miscibility, but in our case, this cannot be observed because of the low content of PP in the blend. However, the observed increase in the damping factor in the amorphous regions of the PE (-90°C to -10°C) for a reactive extruded blend is to be expected since any crosslinking or branching reactions would lead to an increase in blend viscosity. This increase is ascribed to movement of chain segments in the amorphous phase (29). The results of Flocke (30) for a 70/30 mass% PE/PP copolymer show a similar, but stronger, increase of the damping factor in this temperature range.

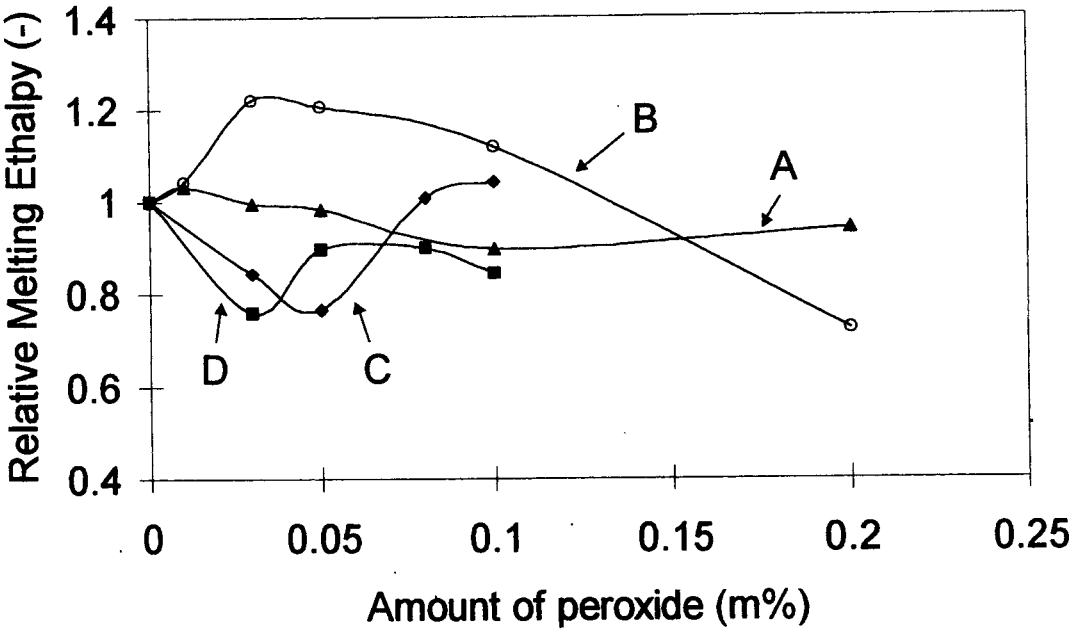

Fig. 14. Relative Melting Enthalpy of HDPE (A with 2 m% BMA, C without monomer) and PP (B with 2 m% BMA, D without monomer).

The relative enthalpies of melting ($\Delta H_{m,rex\ blend}/\Delta H_{m,\ blend}$) of two types of reactive extruded blends are shown in *Fig. 14*. Not only melting enthalpy but also the melting temperature of both the HDPE and the PP are decreased relative to the pure polymers, owing to mutual hindrance in crystallization. Reactive extrusion using peroxide only lowered the relative melting enthalpy, which is a result of a reduction in total crystallinity (31), attributable to the restricted chain mobility resulting from branching and crosslinking reactions in the polyethylene phase, as already concluded from GPC results. The polypropylene peak showed broadening, which can be a result of degradation (20).

The crystallization enthalpy of the polyethylene and the polypropylene in the reactive extruded blend using both peroxide and monomer is increased com-

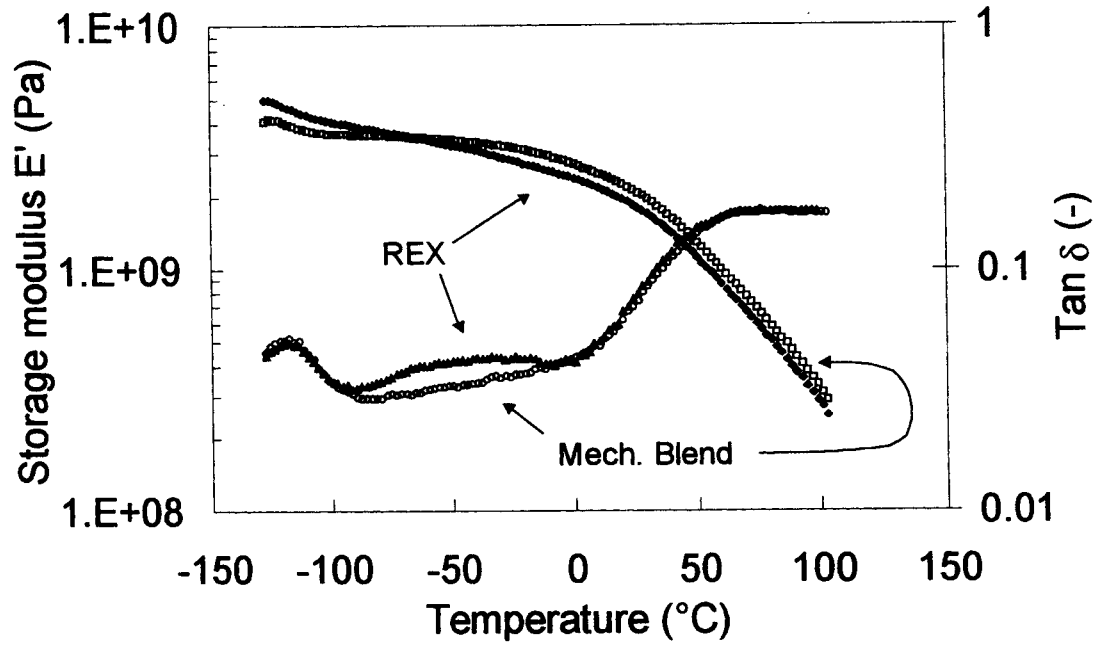

Fig. 15. Storage modulus (E) and damping factor (tanδ), as a function of temperature. Storage modulus (□), tanδ (Δ) for an extruded mixture of HDPE/PP 90/10. Storage modulus (■), tanδ (▲) for a reactive extruded blend of 90 HDPE/ 10 PP with 2 w% BMA and 0.05 w% T101, Co rotating twin screw extruder, Q = 3.6E-3 kg/s, N = 1.8 rps.

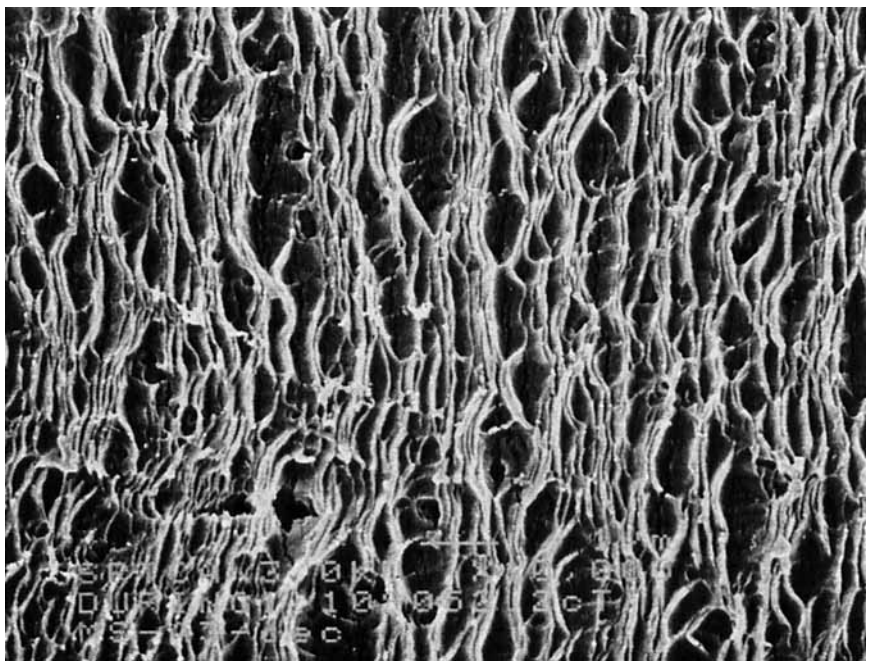

Fig. 16. Scanning electron micrograph of an extruded sample of 90/10 HDPE/PP, co-rotating twin screw extruder, Q = 3.6E-3 kg/s, N = 1.8 rps.

pared with the unmodified blend. Branching can delay the crystallization process, resulting in more time for the polypropylene to crystallize. Another effect comes from the BMA phase, which could act as nucleating center, promote formation of intercrystalline links, and so improve mechanical properties. The domains of the grafted and homopolymerized BMA chains possess a low T_g and act as small rubbery inclusions in the blend, which also improves impact properties.

Electron Microscopy

Scanning electron microscopy has given some insight into the morphology of two blends. Clearly visible in *Fig. 16* is the coarse lamellar structure of the polyethylene in a normal physical mixture. The lamellae are quite thick (0.15 μm) and interlamellar separation is observed. However, the fracture surface of the reactive extruded sample (*Fig. 17*) shows a smaller lamellar thickness and the surface is much more homogeneous. Also, some interconnectivity between the

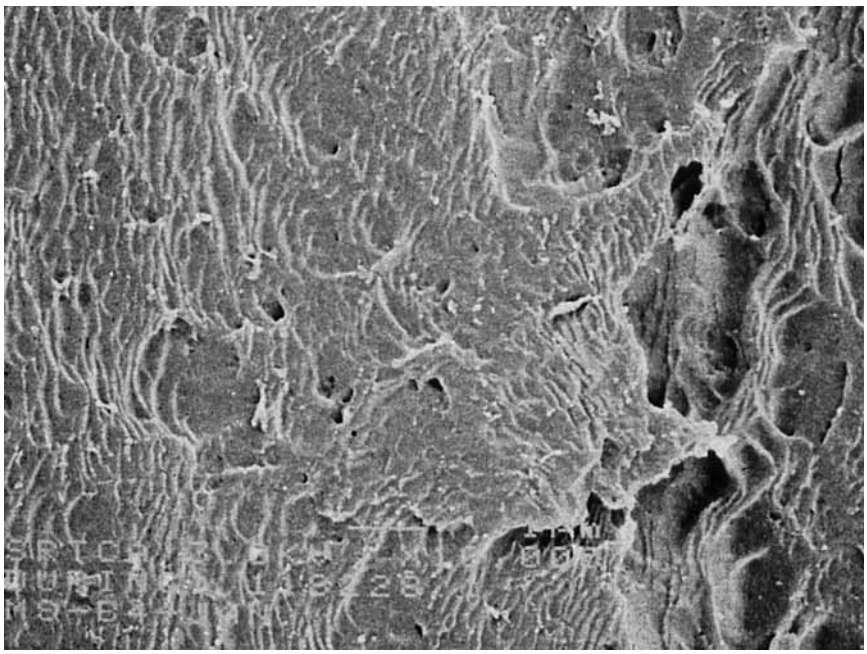

Fig. 17. Scanning electron micrograph of a reactive extruded sample of 90/10 HDPE with 2w% BMA, and 0.05w% T101 co-rotating twin screw extruder, Q = 3.6E-3 kg/s, N = 1.8 rps.

lamellae is observed in the reactive extruded blend. A morphology characterized by small spherulites connected by a large number of bridges provides optimal mechanical properties. Relatively large spherulites with distinct boundaries result in brittleness. Under strain, the boundaries become starting zones for crack development and breakage (32).

CONCLUSIONS

The method of adsorbing a peroxide initiator and n-BMA in a mixture of two polymers not only improves mechanical properties of a blend of amorphous PS with semicrystalline HDPE or PP (33), but also of a blend of two semicrystalline polymers. Physical blends of HDPE with PP result in mixtures that have reduced overall properties. The addition of a peroxide and n-BMA during melt blending of HDPE and PP causes a three-fold increase in elongation at break and doubling of the impact strength. The modulus is generally affected slightly negatively. The addition of a peroxide and n-BMA to a premixed blend of HDPE and PP with a positive displacement pump results in the same effects and comparable final properties as a process where the monomer and initiator are adsorbed in porous PP. The addition of peroxide only has no positive effect on the mechanical properties. Addition of n-BMA only also has negative effects on the final product properties. The most probable toughening mechanisms are a controlled increase in molecular weight, resulting in an improved crystallization behavior, and introduction of a 3rd rubbery phase, resulting from formation of grafted and homopolymerized monomer.

The extrusion conditions are very important for the mechanical properties of a reactive extruded blend. Strong influences are found for screw speed, throughput, and die-resistance. These parameters affect the residence time and temperature of the polymer in the extruder, which influences the conversion of the reaction and the effectiveness of the peroxide, thus providing means for optimization. The co-rotating self-wiping extruder is more suitable for reactive blending than the counter-rotating closely intermeshing one because of the higher attainable shear and longer residence time, and the higher maximal throughput.

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NOMENCLATURE

HDPE	=	High Density Polyethylene.
PP	=	Polypropylene.
ΔH_f	=	Heat of fusion, J/kg.
D	=	Diameter of the extruder screw, m.
E	=	Mixing efficiency.
E'	=	Storage modulus, Pa.
L	=	Length of the extruder, m.
p	=	Viscosity ratio of dispersed phase and matrix phase.
Q	=	Throughput, kg/s.
Q_l	=	Leakage flow, kg/s.
R	=	Gas Constant, J/m^3 K.
$tan\delta$	=	Damping factor.
Tc	=	Crystallization temperature, K.
Tm	=	Melting temperature, K.
$\dot{\gamma}$	=	Shear rate, s^{-1}.
τ 1/2	=	Half-life time of the initiator, s.
ϕ_1, ϕ_2	=	Volume fraction polymer.
v_f	=	Number of fully filled chambers.

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